

## An Electron Diffraction Investigation of Cyclooctane and Cyclotetradeca-1,8-diyne

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The structures of gaseous cyclooctane and cyclotetradeca-1,8-diyne have been studied using electron-diffraction technique. The experimental data for cyclooctane are not compatible with the assumption of any single conformation. To fit the data one has to assume a conformational mixture based on high flexibility of the ring and including asymmetric molecular model species. A complete structure analysis of the electron-diffraction data appears rather comprehensive, and refinements beyond the state of the present work may no doubt be made.

The structure analysis of cyclotetradeca-1,8-diyne appears even more complicated. Also in this case the investigation leads to the conclusion that the molecule in the vapour phase must exhibit a substantial freedom of motion.

### EXPERIMENTAL

Commercial cyclooctane ("puriss") from Fluka AG was used. The sample of cyclotetradeca-1,8-diyne was obtained from Professor J. Dale, University of Oslo. Diffraction photographs were taken in the usual way at nozzle temperatures of about 40°C for cyclooctane and 135°C for cyclotetradeca-diyne. Two camera distances were used (approximately 48 cm and 19 cm), giving intensity data from  $s = 1.5 \text{ \AA}^{-1}$  to  $s = 45 \text{ \AA}^{-1}$ .

At each distance four plates were selected and treated according to the usual procedure at this institute.<sup>1</sup>

### STRUCTURE ANALYSIS

*a) General.* The molecular intensity may be expressed as

$$I(s) = \text{const} \sum A_i(s)/r_i \exp\left(-\frac{1}{2} u_i^2 s^2\right) \sin r_i s$$

*r*: interatomic distance

*u*: root mean-square amplitude of vibration.

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contributions from the C—H and C—C distances through one angle. The remaining broad peaks contain all other C—C distances and most other C—H distances. In this case the structure analysis had to be based entirely on the RD curves.

A nonplanar  $n$ -membered ring ( $n \geq 6$ ) has  $n-6$  degrees of freedom available for molecular deformation due to rotation around the bonds. The rule is concerned only with the freedom associated with torsional motion around single bonds, and it implies that bonds and valence angles are kept constant. For example, cyclohexane should according to the rule have zero degrees of freedom, *i.e.* be "rigid", and cyclooctane should have two degrees of freedom. This means that even when bond distances and valency angles are kept constant, two parameters should be varied in the case of cyclooctane. This fact makes the calculation of all possible conformations a rather cumbersome task.

A relatively simple description of the cyclooctane molecule was adopted, based on only 6 structure parameters: Two bond distances, C—C and C—H, two bond angles,  $\angle$  C—C—C and  $\angle$  H—C—H, and two parameters of torsional molecular deformation. The four inner peaks of the experimental RD curve were used to choose a reasonable set of bond distances and bond angles. The set given in Table 1 was used in all further calculations. A preliminary set

Table 1. Preliminary parameters for cyclooctane.

Structure parameters		$u$ -values (Å)	
C—C bond	1.540 Å	C—C bond	0.050
C—H bond	1.100 Å	C—H bond	0.075
C—C—C angle	116.56°	other C—C	0.060
H—C—H angle	108.0°	other C—H	0.100

of  $u$ -values is also given in the table. It mainly serves as a reasonable basis for calculating theoretical curves. Most  $u$ -values could not be determined with any reasonable accuracy.

On this basis the various cyclooctane conformations and their theoretical RD curves are obtained by varying the two deformation parameters mentioned. (The present calculation deals only with models having the same value throughout the ring for each of the bond distances and valence angles.) The different theoretical RD curves are practically identical up to  $r = 2.8$  Å, and they all fit the experimental curve well in this range. The structure determination therefore had to be based on the outer parts of the RD curve, and the procedure consisted in varying the two torsional parameters to find a conformation or mixture of conformations giving a good fit for  $r > 2.8$  Å.

Hendrickson<sup>3</sup> has given a systematic description of symmetric cyclooctane conformations using the following notation (see p. 4858, Table II and figure on p. 4859 in his article):

I	Crown	symmetry	$D_{4d}$
II	CC ("crown")	»	$C_{2v}$
III	("crown")	»	$D_2$
IV	BC	»	$C_s$
V		»	$C_{2h}$
VI	Chair	»	$C_{2h}$
VII	BB (saddle)	»	$D_{2d}$
VIII	Boat (tub)	»	$D_{3d}$
IX		»	$C_2$

All other conformations are described by Hendrickson as asymmetric, and this notation will be used in the present article as well, although some of the "asymmetric" models may have an element of symmetry. "Asymmetric" crowns, for example, always have a twofold axis.

Theoretical RD curves for the forms I, II, III, IV, and VII are shown in Fig. 2 a–e. The forms II, III, and IV still have one degree of freedom compatible with their symmetry. Thus the curves shown are each based on one single out of a series of conformations. The torsion-angle parameter has in each case been chosen in order to obtain the best fit. In spite of this, none of the calculated curves shows a satisfactory agreement with the experimental curve. Distance calculations showed that the remaining four forms (V, VI, VIII, and IX) give equally bad or even worse fit. The forms VII and VIII are strongly deficient in C–C contribution to the curves around 3.57 Å, compared to the experimental curve. The curve representing model IV may be slightly improved by a different choice of torsional parameter, but it is not possible to get rid of the small peaks at 2.9 Å and 3.9 Å, which are incompatible with the experimental curve. It can further be shown by a systematic trial and error procedure, that any possible mixture of the forms I–IX has to be excluded using comparison of calculated and experimental RD curves as criterion. Finally it can be concluded that no *single* asymmetric conformation could lead to satisfactory agreement, since the best alternatives always give unacceptable peaks similar to those occurring in case of form IV above.

Accordingly the only possibility left must be some sort of mixture of conformations, including asymmetric ones. To be acceptable, such a mixture must lead to a maximum near 3.57 Å on the theoretical RD curve, and smooth minima around 2.9 Å and 4.0 Å.

The asymmetric conformations of cyclooctane may be described by the torsional angles in the ring (here named  $\beta_1$ – $\beta_8$ ). The angles are defined in the range from  $-180^\circ$  to  $180^\circ$  with the *trans* position at  $0^\circ$ . The angle  $\beta_1$  corresponds to the bond  $C_2$ – $C_3$  as an axis of rotation,  $\beta_2$  to  $C_3$ – $C_4$ , and so on. As mentioned, "asymmetric" crowns (in Hendrickson's notation) have a twofold axis of symmetry. This means that  $\beta_i = \beta_{i+4}$ ;  $i = 1, 2, 3, 4$ . If  $\beta_1$  and  $\beta_2$  are chosen as parameters for the torsional deformation,  $\beta_3$  and  $\beta_4$  will be functions of  $\beta_1$  and  $\beta_2$ , since the system has only two degrees of freedom. Unfortunately the functional relations are quite complicated.

It seemed rather attracting to postulate a mixture of conformations, including all possible forms belonging to certain limited structure parameter intervals. For simplicity crown forms were chosen as the first objects of investigation, using  $\beta_1$  and  $\beta_2$  as parameters. It seemed reasonable, on empirical

and practical grounds, to keep  $\beta_1$  constant throughout, just varying  $\beta_2$ . Firstly, contributions to the theoretical RD curve from the distances  $C_1-C_4$  and  $C_5-C_8$  would concentrate around 3.57 Å, by the best choice of  $\beta_1$ . Secondly, contributions to the outer part of the curve from distances varying with  $\beta_2$ , would be smeared out, removing unwanted peaks. Thirdly, a constant  $\beta_1$  greatly simplifies calculation.

The angle  $\beta_2$  was varied in steps of 5°, and theoretical RD curves for the resulting models were added with equal weights. The weights were not varied systematically, but it was seen from the separate contributing curves that no essential improvement could be obtained by introducing a weight factor varying with the torsional angles. The angles  $\beta_3$  and  $\beta_4$  were found numerically for each choice of  $\beta_2$  by an iteration procedure using an IBM 1620 computer. The interval of  $\beta_2$  was taken as large as compatible with the set of distance and bond angle parameters chosen. The best  $\beta_1$  value appeared to be 81.0° corresponding to a  $C_1-C_4$  (and  $C_5-C_8$ ) distance equal to 3.59 Å. The theoretical curve is shown in Fig. 2 f. The contributing models are given in terms of  $\beta$ -values in Table 2. Though the calculated RD curve thus obtained definitely

Table 2. Models contributing to the theoretical RD curve in Fig. 2 f.

Contributing form No.	$\beta_1$	$\beta_2$	$\beta_3$	$\beta_4$	Symmetry
1	81.00°	-94.50°	106.86°	- 94.50°	symmetric, III
2	81.00	-91.00	107.04	- 98.10	asymmetric
3	81.00	-86.00	107.99	-103.70	»
4	81.00	-81.00	109.86	-109.86	symmetric, II
5	81.00	-76.00	113.00	-116.90	asymmetric
6	81.00	-71.00	118.18	-125.49	»
7	81.00	-66.00	128.40	-138.38	»

agrees better with the experimental curve than any of the other alternatives discussed, certain discrepancies remain. Other similar alternatives of very flexible conformations may give at least as good a fit, and more complex conformational mixtures may improve the fit. For example an admixture of 20 % of the saddle form (VII) does not upset the agreement, on the contrary it appears to introduce a slight improvement.

From a theoretical point of view, the choice of a constant  $\beta_1$  seems rather arbitrary. Further, model IV seems at least as promising as a basis for a series of asymmetric models, as do the crown forms. The possibility of variations among the individual C—C-bond lengths, or similar variations among C—H bonds or valence angles, have not been investigated. However, the experimental RD curve indicates that such variations, if present in the molecule, must be small. To elucidate all these problems completely without an insurmountable amount of work, more advanced and specially suited computer programmes have to be developed. Such a complete investigation might show that several distinct conformational mixtures each give an equally

satisfactory fit particularly taken into consideration the great flexibility and large number of parameters introduced by the addition of forms.

The following structure-parameter estimates are obtained directly from the first two peaks of the experimental RD curve:

C—C bond distance	1.540 Å
C—H bond distance	1.107 Å
$u_{CC}$	0.054 Å
$u_{CH}$	0.078 Å

No complete least squares calculation was carried out in this case and error estimates are therefore not included. Our interest is focused on the special conformational problem for which no least squares programme seems possible to use. On the other hand the C—C-bond distance estimate should be approximately as good as usual in electron-diffraction investigations.

Somewhat more uncertain are the distances based upon the next two peaks of the experimental RD curve. However, the value for the valence angle C—C—C given in Table 1 (116–117°) is reasonably accurate, probably better than  $\pm 2^\circ$ , while the H—C—H angle (108°) is determined less accurately.

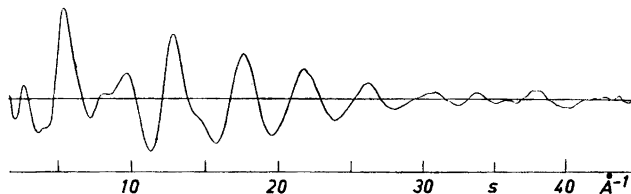


Fig. 3. Cyclotetradecadiyne. Experimental intensity curve.

c) *Cyclotetradeca-1,8-diyne*,  $C_{14}H_{20}$ . The experimental molecular intensity is shown in Fig. 3 and the experimental RD curve with  $k = 0.0015$  in Fig. 5 d. The peak at 1.17 Å contains contributions from the C—H and C≡C bond distances. The peak at 1.52 Å contains all the C—C single bonds, four of them are of the type  $sp-sp^3$  and eight of the type  $sp^3-sp^3$ . The peaks at 2.16 Å and 2.59 Å are mainly composed of C—H distances and C—C distances over one angle (including linear C≡C—C), respectively. The contributions to the remaining peaks will greatly depend on the actual conformation. The structure analysis of this molecule also had to be based on the RD curves.

If the C—C≡C—C groups are assumed linear, the molecule may be described as a ring containing 10 lateral lines. This means four degrees of freedom for the torsional deformation. The molecule was assumed to have four different bond distances: C—H, C≡C, ≡C—C and —C—C—. To get a preliminary and reasonable basis for calculation of models, three different, independent bond angles are assumed, namely  $\angle -C-C-C-$ ,  $\angle \equiv C-C-C$  and  $\angle C-C-H$ . The description of cyclotetradecadiyne thus may be based on 11 structure parameters. A reasonable set of the four bond lengths and the three angles is given in Table 3, together with some preliminary  $u$ -values. This set leads to a good fit between experimental and theoretical RD curves up to 2.8 Å and was used in all further calculations.

Table 3. Preliminary parameters for cyclotetradecadiyne.

Structure parameters			$u$ -values (Å)	
C≡C	bond	1.208 Å	C≡C bond	0.036
≡C-C	bond	1.475 Å	C-C bond	0.050
-C-C-	bond	1.536 Å	C <sub>1</sub> -C <sub>3</sub>	0.050
C-H	bond	1.110 Å	(in C <sub>1</sub> ≡C <sub>2</sub> -C <sub>3</sub> )	
-C-C-C-	angle	114.24°	C-H bond	0.075
≡C-C-C	angle	112.50°	other C-C	0.060
C-C-H	angle	109.04°	other C-H	0.100

Just as for cyclooctane the main problem of the structure determination is to vary the torsional parameters until the best fit between calculated and experimental RD curve is obtained.

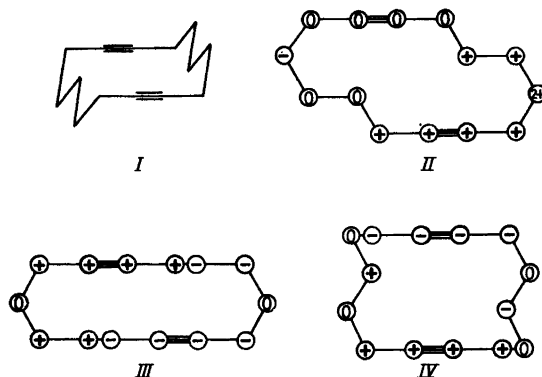


Fig. 4. Cyclotetradecadiyne. Possible conformations without Pitzer strain.

Dale <sup>4,5</sup> has pointed out that the four forms I—IV in Fig. 4 are the only cyclotetradecadiyne forms without Pitzer strain. Therefore they should be energetically preferable compared to other forms. The forms II and III have distance distributions leading to too much area of the RD curve in the interval 2.5 Å—4 Å, while the contribution to the region around 5 Å is too small. Theoretical RD curves for I and IV (slightly improved by torsional deformation) are shown in Fig. 5 b and a. These curves have more and sharper peaks than the experimental curve, indicating the same kind of molecular flexibility in the gas phase as found for cyclooctane. This is quite reasonable in view of the high degree of torsional freedom. The preliminary  $u$ -values for the long distances were probably chosen too small. Larger  $u$ -values were also tried but they did not change the general appearance of the theoretical curves very much.

Since the structure analysis of cyclotetradecadiyne is even more complex than that of cyclooctane, the approach had to be less systematic, and the

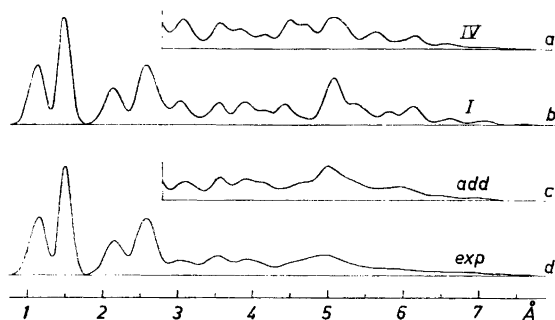


Fig. 5. Cyclotetradecadiyne. RD curves,  $k = 0.0015$ . a–c theoretical; d experimental.

choices of trial structures were made more at random but all the time with the aim of best fit between calculated and experimental RD curves. Among the conformations and conformational mixtures tried, one is perhaps worth mentioning, the calculated RD curve of which is shown in Fig. 5 c. The example is based upon model I (Fig. 4). The two linear parts C—C≡C—C are rotated around an axis through the centers of the two tripple bonds and in opposite direction without destroying the twofold symmetry around this axis. The RD curve in Fig. 5 c is based on all forms in a certain rotational angle interval, centered around the value of  $44^\circ$  for the angle between the two C—C≡C—C groups. The interval is not sharply determined from this method of calculation, but is found to be about  $30^\circ$  to  $40^\circ$  broad (corresponding to an angle interval of approximately  $25^\circ$ – $60^\circ$ ). This RD curve was the best one obtained in this investigation.

A more complete investigation of this molecule would be rather complicated, and it seems probable that several conformational mixtures may lead to satisfactory fit if enough parameters are varied and enough forms are involved. However, the physical significance of such results would be doubtful.

It was not possible in this investigation to make better estimates of distances and  $u$ -values, than the preliminary set given in Table 3.

#### DISCUSSION

The results of this investigation indicate strongly that cyclooctane and cyclotetradeca-1,8-diyne are highly flexible molecules in the gas phase at the temperatures of the experiments. This conclusion is in harmony with Hendrickson's<sup>3</sup> statement about cyclooctane: "... all of the above forms are probably readily interconvertible. This also suggests that, as one form of cyclooctane is not clearly favoured energetically as in cyclohexane or cycloheptane, cyclooctane will resemble cyclopentane in being a very mobile conformational mixture at ordinary temperatures."

An earlier electron-diffraction investigation of cyclooctane<sup>6</sup> concluded that a crown type structure was in agreement with the diffraction data, but



up to 40 % admixture of other forms was possible. The bond distance C—C was found to be  $1.55 \pm 0.03$  Å and  $\angle$  C—C—C  $116^\circ$ , in agreement with the present investigation.

Dale <sup>7,8</sup> gives some arguments favouring the saddle conformation of cyclooctane. This form is much too compact to fit the experimental data of this investigation, but, as mentioned, up to 20 % admixture of saddle form is possible, without destroying the fit obtained.

It is of interest to compare the present results from gas electron-diffraction studies with results from X-ray crystallography. In the solid state the conformational choice is of course influenced by the lattice forces. This means that in the crystal one single conformation may be chosen for a molecule for which a conformational mixture is found in the gas phase. Further the various cyclooctane derivatives may choose different conformations in the crystal according to the position and the type of the substituent. Dunitz and Mugnoli <sup>9</sup> have studied cyclooctane-1,2-*trans*-dicarboxylic acid, and Groth <sup>10</sup> has studied 3,6-spirodecyclooctylidene-1,2,4,5-tetraoxa-cyclohexane. For both these molecules the X-ray study results in form IV for the eight-membered ring.

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